

On The Isostructural And Superprotonic $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$ Transformations: Physical Or Chemical Nature?

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Abstract

For over 20 years, researchers have agreed that when pentacesium trihydrogen tetrasulfate hydrate ($\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$) is heated through 141 °C, the observed conductivity increase corresponds to a physical transformation: a first-order superprotonic phase transition. A careful high-temperature phase behavior examination of this acid salt was performed by means of simultaneous thermogravimetric and differential scanning calorimetry, conventional and modulated differential scanning calorimetry, and impedance spectroscopy. The results present evidence that this transformation is of chemical, instead of physical nature. The conductivity increase is an exclusive consequence of a partial thermal decomposition, where liquid water (dissolving part of the surface salt) and hygroscopic cesium pyrosulfate ($\text{Cs}_2\text{S}_2\text{O}_7$), as decomposition products, behave like a polymer electrolyte membrane where the proton transport mechanism includes the vehicle type, using hydronium (H_3O^+) as a charge carrier. Additionally, it was found that the intermediate temperature transformation (so-called isostructural phase transition) at around 87 °C is also of chemical nature.

Keywords

$\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$; Isostructural Phase Transition; Superionic Conductor; Superprotonic Phase Transition; Thermal Surface Decomposition